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Two- and Four-Coordinate Gold(I) Complexes of Tris(2-(diphenylphosphino)ethyl)phosphine[†]

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Treatment of tris(2-(diphenylphosphino)ethyl)phosphine (PP_3) with Me_2SAuCl produces colorless $[Au_2(\mu\text{-}PP_3)_2]Cl_2$. This crystallizes as a dichloroform solvate in the triclinic space group $P\bar{1}$ (No. 2) with a = 13.389 (4) Å, b = 14.924 (4), c = 24.441 (8) Å, α = 72.41 (2)°, β = 74.75 (2)°, and γ = 69.22 (2)° at 130 K with Z = 2. Refinement of 8626 reflections and 507 parameters yields R = 0.052 and R_w = 0.054. The salt contains a binuclear cation in which each PP_3 coordinates through three phosphorus atoms to one gold(I), while one arm forms a bridge to the other gold(I). The two golds are widely separated by 6.199 Å. Both have roughly tetrahedral geometry. The binuclear ion is resistant to reaction with the nucleophiles azide and thiocyanate but reacts readily with Me_2SAuCl to form $Au_4Cl_4(\mu\text{-}PP_3)$. Colorless needles of the dichloromethane/ethyl ether solvate of $Au_4Cl_4(\mu\text{-}PP_3)$ crystallize in the monoclinic space group $P2_1/n$ (No. 14) with a = 25.393 (15) Å, b = 15.717 (13) Å, c = 27.565 (16) Å, and β = 106.16 (4)° at 130 K with Z = 4. Refinement of 3789 reflections and 368 parameters yields R = 0.082 and R_w = 0.074. There are two similar $Au_4Cl_4(\mu\text{-}PP_3)$ molecules in the asymmetric unit. Each phosphorus in part of a nearly linear PAuCl moiety. While there are no Au–Au contacts less than 3.5 Å within either independent molecule, there are short contacts of 3.1 Å between molecules.

Introduction

Gold(I) complexes frequently exist as linear, two-coordinate species.[1] Three-coordinate and four-coordinate complexes are less common. The observation that a number of simple gold(I) complexes of phosphine ligands, including two-, three-, and four-coordinate forms, have significant antitumor activities has increased interest in these species.[2] It has been suggested that the phosphines themselves are the cytotoxic agents and that the metal ion/phosphine complex serves to protect the reagent during delivery to the appropriate target.[2] For complexes with chelating ligands, such as tetrahedral $[Au(dppe)_2]^+$, chelate ring opening is expected to be a critical step in the mode of antitumor action.[3]

In this context, it appears to be important to learn about the factors that allow four-coordinate, tetrahedral gold(I) complexes to form with various phosphine ligands. Relatively few such species are known. Those that have been structurally examined include $[Au(PPh_3)_4][(BPh_4)]$,[4] $[Au(PPh_2Me)_4][PF_6]$,[5] $[Au(dppe)_2]^+$ as its hexafluoroantimonate[6] and chloride salts,[7] and $[Au(dpma)_2][Au(CN)_2]$.[8] Much attention has been given to designing phosphine ligands for a variety of different geometrical purposes, such as promoting planar coordination,[9] producing asymmetric hydrogenation catalysts,[10] and constructing polynuclear complexes.[11] In contrast, little attention has been given to exploring the relationship of phosphine structural elements in producing tetrahedral complexes.

Here, we report on one such study in which we have explored the coordination of the potentially tetradentate tetraphosphine tris(2-(diphenylphosphino)ethyl)phosphine (PP_3) with gold(I).

Results

Treatment of a dichloromethane solution of PP_3 with 1 molar equiv of Me_2SAuCl in dichloromethane gives a colorless solution from which colorless crystals of $[Au_2(\mu\text{-}PP_3)_2]Cl_2$ are obtained in 96% yield after the gradual addition of diethyl ether.

The structure of the binuclear cation as determined by an X-ray crystal structure is shown in Figure 1. Selected atomic coordinates are given in Table I, and bond distances and angles are shown in Table II. The complex crystallizes with one cation, two chloride ions, and three chloroform molecules in the asymmetric unit. There are no unusual contacts between these. The chloride ions are not coordinated to the gold ions; the shortest Au···Cl distance is 6.714 Å.

Table I. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $[Au_2(\mu\text{-}PP_3)_2]Cl_2{\cdot}2CHCl_3$[a]

	x	y	z	U
Au(1)	5395 (1)	−2056 (1)	8098 (1)	20 (1)[b]
Au(2)	2655 (1)	2040 (1)	6887 (1)	17 (1)[b]
P(1)	5622 (3)	−542 (2)	8127 (1)	20 (1)[b]
P(2)	5403 (3)	−2525 (2)	9131 (1)	21 (1)[b]
P(3)	7149 (3)	−2292 (2)	7470 (1)	22 (1)[b]
P(4)	2642 (2)	1986 (2)	7853 (1)	18 (1)[b]
P(5)	3384 (3)	670 (2)	6421 (1)	20 (1)[b]
P(6)	980 (3)	2355 (2)	6564 (1)	20 (1)[b]
P(7)	3919 (3)	2767 (2)	6102 (1)	18 (1)[b]
P(8)	4036 (3)	−2204 (2)	7727 (1)	21 (1)[b]
Cl(7)	6524 (3)	1447 (3)	4516 (1)	34 (1)[b]
Cl(8)	5815 (3)	1618 (2)	8985 (1)	32 (1)[b]
C(73)	5669 (10)	−690 (8)	8888 (5)	21 (3)
C(74)	4956 (10)	−1322 (8)	9307 (5)	23 (3)
C(75)	6960 (9)	−505 (8)	7707 (5)	20 (3)
C(76)	7762 (10)	−1519 (8)	7656 (5)	25 (3)
C(77)	4779 (9)	710 (8)	7894 (5)	23 (3)
C(78)	3618 (9)	866 (8)	8210 (5)	19 (2)
C(79)	2254 (9)	624 (8)	6142 (5)	20 (3)
C(80)	1373 (10)	1620 (8)	6019 (5)	25 (3)
C(81)	4385 (9)	1004 (8)	5777 (5)	22 (3)
C(82)	4144 (10)	2134 (8)	5530 (5)	21 (3)
C(83)	4068 (9)	−623 (8)	6715 (5)	22 (3)
C(84)	3336 (10)	−1092 (8)	7226 (5)	24 (3)

[a] Phenyl carbons and chloroform positions omitted; see supplementary material. [b] Equivalent isotropic U defined as one-third of the trace of the orthongalized U_{ij} tensor.

Table II. Selected Interatomic Distances and Angles for $[Au_2(\mu\text{-}PP_3)_2]Cl_2{\cdot}2CHCl_3$

	Distances (Å)		
Au(1)–P(1)	2.408 (4)	Au(2)–P(5)	2.417 (3)
Au(1)–P(2)	2.410 (3)	Au(2)–P(6)	2.415 (4)
Au(1)–P(3)	2.417 (3)	Au(2)–P(7)	2.461 (3)
Au(1)–P(8)	2.335 (4)	Au(2)–P(4)	2.332 (3)
	Angles (deg)		
P(1)–Au(1)–P(2)	85.6 (1)	P(5)–Au(2)–P(6)	86.7 (1)
P(1)–Au(1)–P(3)	84.9 (1)	P(d)–Au(2)–P(7)	84.4 (1)
P(1)–Au(1)–P(8)	126.3 (1)	P(5)–Au(2)–P(4)	126.8 (1)
P(2)–Au(1)–P(3)	116.2 (1)	P(6)–Au(2)–P(7)	110.7 (1)
P(2)–Au(1)–P(8)	120.9 (1)	P(6)–Au(2)–P(4)	120.2 (1)
P(3)–Au(1)–P(8)	115.0 (1)	P(7)–Au(2)–P(4)	119.4 (1)

The cation consists of two gold ions that are each coordinated by three phosphorus atoms of one ligand and by another phosphorus atom of the other ligand. The bridging arms of the PP_3 ligands produce a ten-membered ring that incorporates the two

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[†] Abbreviations: dppe, 1,2-bis(diphenylphosphino)ethane; dpma, bis((diphenylphosphino)methyl)phenylarsine; PP_3, tris(2-(diphenylphosphino)ethyl)phosphine.

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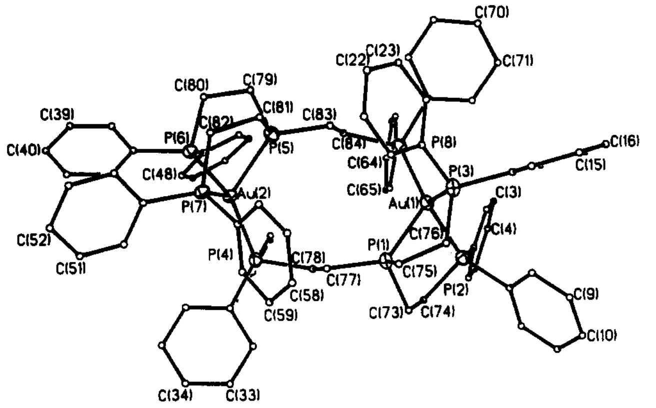

Figure 1. The cation in $[Au_2(\mu\text{-}PP_3)_2]Cl_2$ showing 50% thermal contours for heavy atoms and uniform, arbitrarily sized circles for other atoms.

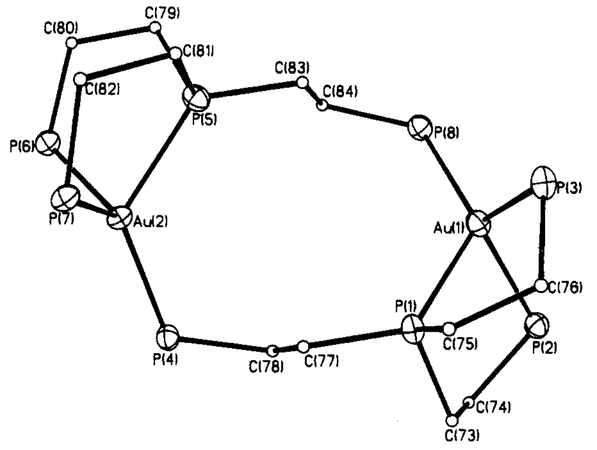

Figure 2. Core of the $[Au_2(\mu\text{-}PP_3)_2]^{2+}$ structure with the phenyl rings removed.

gold ions. This is more readily visualized by examining Figure 2, which shows the core of the cation without the phenyl rings. Within this ring, the two gold ions are relatively remote from one another. The nonbonded Au···Au distance within the ion is 6.199 Å.

Each gold ion has roughly tetrahedral geometry. The structural parameters at the two independent sites within the cation are remarkably similar. In each, the Au–P distances which involve the unique phosphorus atoms P(8) or P(4) that come from the bridging arm average 2.334 Å and are 0.087 Å shorter than the average of the other Au–P distance (2.412 Å). Moreover, these distances are shorter than the range of Au–P distances (2.38–2.56 Å) seen for other tetrahedral phosphine/gold(I) complexes.[4-8]

The angular distortion within the coordination sphere of each gold can readily be identified with specific structural elements. The most constricted P–Au–P angles are the four that involve the five-membered chelate rings. All of these angles are less than 90°. The most open P–Au–P angles are those (P(1)–Au(1)–P(8) and P(4)–Au(2)–P(5)) that are a part of the ten-membered ring. In considering the angular disposition of phosphorus atoms at both gold ions, it is important to note that the largest difference between comparable angles is only 5.5°. Thus, although there are two independent gold ions within the cation, both have very similar geometries.

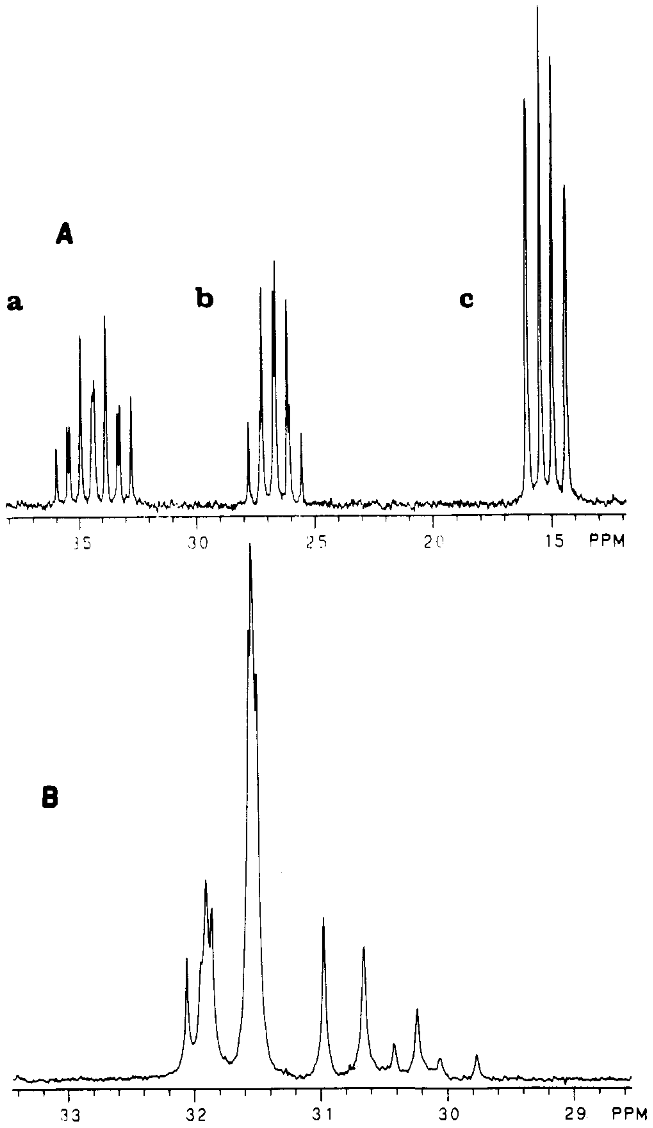

Figure 3. 122-MHz $^{31}P\{^1H\}$ NMR spectra of (A) $[Au_2(\mu\text{-}PP_3)_2]Cl_2$ in chloroform at 23 °C and (B) $Au_4Cl_4(\mu\text{-}PP_3)$ in chloroform at 23 °C. Multiplet assignments are given in the text.

The cation retains its binuclear structure in solution. Figure 3 shows the $^{31}P\{^1H\}$ NMR spectrum of the complex in chloroform solution at 22 °C. Three multiplets of relative intensity 1:1:2 are observed. This indicates that normal mobility available in solution renders the two gold ions and the two phosphine ligands equivalent. As labeled in trace A of Figure 3, multiplet a is assigned to the internal phosphorus atoms (P(1) and P(5) of Figure 1), multiplet b is assigned to the terminal atoms of the bridging arms (P(4) and P(8)), and multiplet c is assigned to the four terminal phosphines that do not participate in bridging (P(2), P(3), P(6), and P(7)). The spectrum has been analyzed as an AMX_2 system to yield $\delta_c = 15.2$ ppm for the four terminal phosphorus atoms (P(2), P(3), P(6), and P(7)), $\delta_a = 34.4$ ppm for the two internal phosphorus atoms (P(1) and P(5)), and $\delta_b = 26.7$ ppm for the phosphorus atoms (P(4) and P(8)) of the bridging arms with a 130-Hz coupling constant within the chelate ring (i.e., *J*(P(1), P(2)) etc.), a 70-Hz coupling between unlike terminal phosphorus atoms (i.e., *J*(P(2), P(8)) etc.), and a 66-Hz coupling between the internal phosphorus atom and the phosphorus of the bridging arm (i.e., *J*(P(1), P(8)) etc.).

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Table III. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $[Au_4Cl_4(\mu\text{-}PP_3)]\cdot 2.8CH_2Cl_2\cdot(CH_3CH_2)_2O^a$

	x	*y*	*z*	*U*
Au(1)	6110 (1)	4640 (2)	1993 (1)	34 (1)[b]
Au(2)	7589 (1)	−503 (2)	2247 (1)	47 (2)[b]
Au(3)	9200 (1)	2939 (2)	2736 (1)	23 (1)[b]
Au(4)	7267 (1)	2242 (2)	422 (1)	28 (1)[b]
Au(5)	8197 (1)	3185 (2)	144 (1)	23 (1)[b]
Au(6)	8366 (1)	2829 (2)	−2162 (1)	18 (1)[b]
Au(7)	7326 (1)	−724 (2)	−2171 (1)	20 (1)[b]
Au(8)	6454 (1)	5214 (2)	−2565 (1)	26 (1)[b]
Cl(1)	6209 (8)	5534 (14)	2684 (7)	41 (6)
Cl(2)	7854 (10)	−1804 (16)	2057 (9)	70 (8)
Cl(3)	9124 (8)	2883 (14)	3543 (7)	39 (6)
Cl(4)	7004 (7)	1875 (13)	−410 (7)	35 (6)
Cl(5)	7661 (8)	4288 (14)	298 (7)	43 (6)
Cl(6)	8982 (7)	3034 (12)	−2629 (6)	25 (5)
Cl(7)	7931 (7)	−1771 (12)	−1824 (7)	27 (5)
Cl(8)	6139 (8)	5628 (14)	−3399 (7)	39 (6)
P(1)	5921 (8)	3863 (13)	1277 (7)	22 (6)
P(2)	7275 (10)	729 (17)	2436 (9)	51 (7)
P(3)	9240 (8)	3058 (14)	1929 (7)	31 (5)
P(4)	7441 (8)	2530 (13)	1246 (7)	23 (6)
P(5)	8705 (8)	2245 (15)	−111 (7)	29 (6)
P(6)	7774 (8)	2595 (13)	−1714 (7)	26 (6)
P(7)	6812 (8)	413 (13)	−2472 (7)	20 (5)
P(8)	6709 (8)	4853 (13)	−1757 (7)	21 (5)
C(73)	6386 (31)	2964 (55)	1251 (29)	50
C(74)	6992 (32)	3411 (54)	1387 (30)	50
C(75)	7510 (27)	1846 (46)	2139 (25)	28 (21)
C(76)	7435 (32)	1534 (54)	1602 (30)	50
C(77)	8615 (27)	2522 (45)	1494 (26)	27 (21)
C(78)	8155 (25)	3076 (43)	1600 (22)	13 (18)
C(79)	8343 (33)	1775 (55)	−751 (30)	50
C(80)	8126 (31)	2691 (56)	−987 (29)	50
C(81)	7502 (33)	1420 (54)	−1823 (30)	50
C(82)	7214 (24)	1376 (41)	−2432 (22)	9 (18)
C(83)	7180 (32)	3144 (54)	−1847 (30)	50
C(84)	7369 (32)	4083 (53)	−1593 (30)	47 (26)

[a] Phenyl carbons omitted; see supplementary material. [b] Equivalent isotropic *U* defined as one-third of the trace of the orthongalized $\mathbf{U}_{ij}$ tensor.

Table IV. Selected Bond Distances and Angles for $Au_4Cl_4(\mu\text{-}PP_3)$

Distances (Å)			
Au(1)–Cl(1)	2.33 (2)	Au(5)–Cl(5)	2.31 (2)
Au(2)–Cl(2)	2.26 (3)	Au(6)–Cl(6)	2.31 (2)
Au(3)–Cl(3)	2.29 (2)	Au(7)–Cl(7)	2.27 (2)
Au(4)–Cl(4)	2.28 (2)	Au(8)–Cl(8)	2.31 (2)
Au(1)–P(1)	2.26 (2)	Au(5)–P(5)	2.20 (2)
Au(2)–P(2)	2.21 (3)	Au(6)–P(6)	2.22 (2)
Au(3)–P(3)	2.26 (2)	Au(7)–P(7)	2.23 (2)
Au(4)–P(4)	2.23 (2)	Au(8)–P(8)	2.21 (2)
Angles (deg)			
Cl(1)–Au(1)–P(1)	173.1 (7)	Cl(5)–Au(5)–P(5)	171.1 (8)
Cl(2)–Au(2)–P(2)	175.9 (9)	Cl(6)–Au(6)–P(06)	178.5 (7)
Cl(3)–Au(3)–P(3)	176.7 (8)	Cl(7)–Au(7)–P(7)	173.1 (7)
Cl(4)–Au(4)–P(4)	173.7 (8)	Cl(8)–Au(8)–P(8)	176.3 (8)

$[Au_2(\mu\text{-}PP_3)_2]Cl_2$ appears to be more susceptible to attack by electrophiles than by nucleophiles. It reacts readily with Me_2SAuCl in dichloromethane solution at 22 °C according to eq 1. $Au_4Cl_4(\mu\text{-}PP_3)$ is readily isolated as colorless crystals by adding diethyl ether to the solution. In contrast, no reaction was observed when $[Au_2(\mu\text{-}PP_3)_2]Cl_2$ was treated with either sodium azide or sodium thiocyanate in a mixture of dichloromethane and methanol. $[Au_2(\mu\text{-}PP_3)_2]Cl_2$ can also be prepared by the addition of 4 equiv of Me_2SAuCl to PP_3 in dichloromethane. It has been prepared previously.[12]

$$[Au_2(\mu\text{-}PP_3)_2]Cl_2 + 6Me_2SAuCl \rightarrow 2Au_4Cl_4(\mu\text{-}PP_3) \quad (1)$$

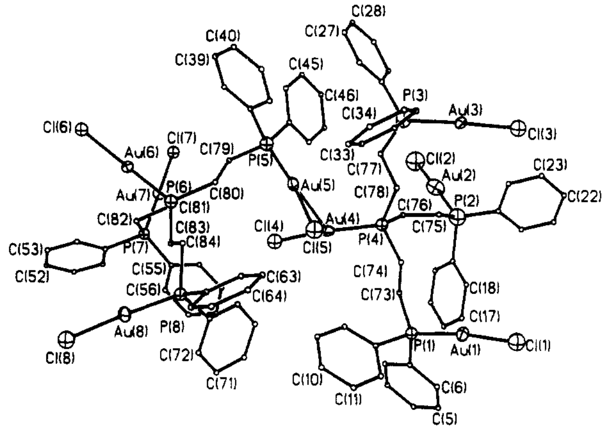

Figure 4. Perspective view of both molecules of $Au_4Cl_4(\mu\text{-}PP_3)$ showing the interaction between them within the asymmetric unit.

The structure of $Au_4Cl_4(\mu\text{-}PP_3)$ has been determined by X-ray diffraction. An abbreviated list of atomic coordinates is given in Table III. Selected bond distances and angles are given in Table IV. There are two molecules of $Au_4Cl_4(\mu\text{-}PP_3)$, 2.8 molecules of dichloromethane, and one molecule of ethyl ether in the asymmetric unit. A perspective view of both molecules of $Au_4Cl_4(\mu\text{-}PP_3)$ is given in Figure 4. Within each molecule an AuCl unit is attached to each phosphorus atom to give nearly linear P–Au–Cl units. The dimensions within these portions are entirely normal.[13,14] The average Au–P distance of 2.23 Å reflects the expected shortening upon reduction of the coordination number to 2. There are no close contacts between gold ions within either molecule. However, there are short Au–Au contacts between molecules. Figure 4 shows the contact between Au(4) and Au(5), which is 3.061 (5) Å long. Another interaction, not shown in Figure 4, involves contacts between Au(6) and Au(7) of another molecule. This Au(6)–Au(7) distance is 3.140 (5) Å, whereas the intramolecular Au(6)–Au(7) spearation is 6.175 Å. It has been noted that contacts of less than 3.5 Å between ions as large as gold(I) must be considered to reflect a chemical interaction between these ions and such short contacts are common in the structures of two-coordinate gold(I) complexes.[14-16]

The $^{31}P\{^1H\}$ NMR spectrum of $Au_4Cl_4(\mu\text{-}PP_3)$ is shown in trace B of Figure 3. Analysis of the second-order spectrum as an AB_3 system yields $\delta_1 = 31.6$ ppm for the three terminal phosphorus atoms and $\delta_2 = 30.4$ ppm for the internal phosphorus atoms with a 36.1-Hz coupling between them and a small, but non-zero, coupling between the terminal phosphorus atoms.

Discussion

The tetradentate ligand PP_3 has been shown to function as a tripodal ligand, capable of spanning four contiguous coordination sites in trigonal-bipyramidal, square-pyramidal, and octahedral complexes.[17] However, with tetrahedral Au(I) it prefers to act in a different fashion involving both chelation and bridging. A similar structure was previously postulated on the basis of ^{31}P NMR evidence for the nickel(0) complex $Ni_2(\mu\text{-}PP_3)_2$.[18] However, the related nickel(0) compound $Ni\{N(CH_2CH_2PPh_2)_3\}$, $Ni(NP_3)$, is strictly monomeric, with the nitrogen and all three phosphorus atoms connected to a single nickel atom.[19] The difference between the structures of these nickel complexes has

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been attributed to ring strain that originates in the longer Ni–P vs Ni–N distances.[18] This ring strain may also be operating in $[Au_2(\mu\text{-}PP_3)_2]^{2+}$, since the P–Au–P angles within the chelate portion are well below what is ideal for a tetrahedrally coordinated metal ion. Ring strain in $[Au_2(\mu\text{-}PP_3)_2]^{2+}$ is somewhat reduced by having one atom of each PP_3 form a bridge to the adjacent gold(I). This gives a binuclear complex in which the phosphorus donors as a whole are more uniformly distributed about each gold(I).

This binuclear complex appears to be robust. It does not react with thiocyanate or azide, but it is susceptible to attack by an electrophile (Me_2SAuCl). We suspect that this attack occurs when one of the chelate rings is opened. This exposes a phosphorus lone pair on the free arm. This lone pair is vulnerable to reaction with the external electrophile. On the other hand, the remaining three-coordinate gold is not particularly susceptible to nucleophilic attack. It is three-coordinate and relatively electron rich when compared to the large number of two-coordinate gold(I) complexes that are known. Thus it resists addition of another nucleophile. The product of electrophilic attack is $Au_4Cl_4(PP_3)$, a complex that has been prepared previously and has some antitumor activity.[12]

Experimental Section

Preparation of Compounds. (Dimethyl sulfide)gold(I) chloride[20] was prepared by an established route, and tris(2-(diphenylphosphino)ethyl)phosphine (PP_3) was purchased from Strem Chemicals. Both of the new compounds were synthesized in air, and the pure complexes are air-stable both as solids and in solution.

$[Au_2(\mu\text{-}PP_3)_2]Cl_2$. A solution of 54.5 mg (0.185 mmol) of Me_2SAuCl in a minimum volume of dichloromethane was added to a solution of 124.1 mg (0.185 mmol) of PP_3 in a minimum volume of dichloromethane. The solution was stirred, and after 30 min ethyl ether was added dropwise. The white precipitate was collected by filtration and washed with ethyl ether. The product may be recrystallized by dissolution in dichloromethane and precipitation by the addition of ethyl ether. Yield: 159.8 mg (96%).

$[Au_4Cl_4(\mu\text{-}PP_3)]$. Method 1. A solution of 23.9 mg (0.0811 mmol) of Me_2SAuCl in a minimum volume of dichloromethane was added to a solution of 24.3 mg (0.0134 mmol) of $[Au_2(\mu\text{-}PP_3)_2]Cl_2$ in a minimum volume of dichloromethane. The solution was allowed to stir for 30 min. A white, crystalline product was obtained by the addition of ethyl ether. The product was recrystallized by dissolution in dichloromethane and precipitation by the addition of ethyl ether. Yield: 24.0 mg (56%).

Method 2. A solution of 43.8 mg (0.149 mmol) of Me_2SAuCl in a minimum volume of dichloromethane was added to a solution of 25.8 mg (0.0385 mmol) of PP_3 in a minimum volume of dichloromethane. The solution was allowed to stir for 30 min. The white, crystalline product was obtained by the addition of ethyl ether. The product was recrystallized by dissolution in dichloromethane and precipitation by the addition of ethyl ether. Yield: 28.2 mg, (47.4%).

X-ray Data Collection. $[Au_2(\mu\text{-}PP_3)_2]Cl_2\cdot 2CHCl_3$. Colorless needles were formed by slow diffusion of ethyl ether into a chloroform solution of $[Au_2(\mu\text{-}PP_3)_2]Cl_2$. The crystals were removed from the diffusion tube and rapidly coated with light hydrocarbon oil to reduce loss of solvent from the crystal. The crystal was mounted in the cold stream of a Syntex $P2_1$ diffractometer equipped with a modified LT-1 low-temperature apparatus. Unit cell dimensions were obtained from a least-squares fit of 10 reflections with $12° \le 2\theta \le 23°$. No decay in the intensities of two standard reflections occurred during data collection. Data collection parameters are summarized in Table V.

$2[Au_4Cl_4(\mu\text{-}PP_3)]\cdot 2.8CH_2Cl_2\cdot (CH_3CH_2)_2O$. Colorless needles were formed by slow diffusion of ethyl ether into a dichloromethane solution of $[Au_4Cl_4(\mu\text{-}PP_3)]$. The unit cell parameters were obtained from a least-squares fit of 21 reflections with $12° \le 2\theta \le 37°$. The space group $P2_1/n$ (No. 14) was uniquely determined by the observed conditions: $h0l$, $h + l = 2n$; $0k0$, $k = 2n$. Only random fluctuations (less than 2%) were observed in the intensities of two standard reflections during data collection. Data collection parameters are summarized in Table V. All other data collection procedures were identical with those of $[Au_2(\mu\text{-}PP_3)_2]Cl_2\cdot 2CHCl_3$.

Solution and Refinement of the Structures. $[Au_2(\mu\text{-}PP_3)_2]Cl_2\cdot 2CHCl_3$. All structure determination and refinement calculations were done on a Data General Eclipse MV/10000 computer using the SHELXTL version 5.1 software package. The positions of the two gold atoms were generated from FMAP8, the Patterson-solving routine of SHELXTL. All other atom positions were located from the successive difference maps. Anisotropic thermal parameters were assigned to the gold, phosphorus, and chlorine atoms. All hydrogen atoms were included at calculated positions by using a riding model, in which the C–H vector was fixed at 0.96 Å and the isotropic thermal parameter for each hydrogen atom was given a value 20% greater than the carbon atom to which it was bonded. Scattering factors and corrections for anomalous dispersions were taken from a standard source.[21] The final stages of refinement included an absorption correction.[22] The final R value of 0.052 was computed with a data-to-parameter ratio of 17.0. This yielded a goodness-of-fit of 1.004 and a maximum shift/esd of −0.026 for x of C(54) in the last cycle of refinement. A value of 1.69 e/Å^3 was found as the largest feature on the final difference Fourier map. This peak was located 0.99 Å from Au(1). The weighting scheme used was $w = \sigma^2(F_o)^{-1}$. Corrections for anomalous dispersions were applied to all atoms.

Table V. Crystal Data and Data Collection Parameters for $[Au_2(\mu\text{-}PP_3)_2]Cl_2\cdot 2CHCl_3$ (**1**) and $2Au_4Cl_4(\mu\text{-}PP_3)\cdot 2.8CH_2Cl_2\cdot 0.2(CH_3CH_2)_2O$ (**2**)

	1	**2**
formula	$C_{86}H_{86}Au_2Cl_8P_8$	$C_{90.8}H_{99.6}Au_8Cl_{13.6}OP_8$
fw	2044.99	3512.67
color and habit	colorless needles	colorless needles
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a, Å	13.389 (4)	25.393 (15)
b, Å	14.924 (4)	15.717 (13)
c, Å	24.441 (8)	27.565 (16)
α, deg	72.41 (2)	90
β, deg	74.75 (2)	106.16 (4)
γ, deg	69.22 (2)	90
V, Å^3	4286 (2)	10 566 (12)
T, K	130	130
Z	2	4
cyrst dimens, mm	0.10 × 0.18 × 0.45	0.075 × 0.075 × 0.375
d_{calcd}, g cm^{-3}	1.59	2.21
λ(Mo Kα), Å	0.71069	0.71069
μ(Mo Kα), cm^{-1}	38.54	115.56
range of transm factors	0.44–0.46	0.36–0.47
no. of data used in refinement [$I > 3\sigma(I)$]	8626	3798
no. of params refined	507	368
R^a	0.052	0.082
$R_w{}^b$	0.054	0.074

$^a R = \sum||F_o| - |F_c||/|F_o|$. $^b R_w = \sum||F_o| - |F_c||w^{1/2}/\sum|F_o w^{1/2}|$, where $w = 1/\sigma^2(F_o)$.

$2[Au_4Cl_4(\mu\text{-}PP_3)]\cdot 2.8CH_2Cl_2\cdot (CH_3CH_2)_2O$. The positions of the eight gold atoms were generated by direct methods. Other atom positions were located from successive difference Fourier maps. Phenyl rings were refined as rigid hexagons with the C–C distance fixed at 1.39 Å. Anisotropic thermal parameters were assigned to all the gold atoms. The C(86)–Cl(11) and C(86)–Cl(12) distances were fixed at 1.7 Å. Carbon–carbon and carbon–oxygen distances were fixed within the diethyl ether molecule, which was translationally disordered with C(88B) and C(89B) in close proximity to the disordered dichloromethane molecule. The site occupancies of C(86), Cl(11), Cl(12), C(88A), and C(89A) were refined as a variable to 81.2%. Thus, C(88B) and C(89B) have site occupancies of 18.8%, while C(90), C(91), and O have 100% occupancy. The thermal parameters for O, C(23), C(32), C(43), C(44), C(49), C(62), C(73), C(74), C(76), C(78), C(80), C(81), C(82), and C(86) were fixed at 0.050 during refinement. Scattering factors and corrections for anomalous dispersions were taken from a standard source.[21] The final stages of refinement included an absorption correction.[22] Due to the dominance of scattering by heavy atoms, hydrogen atoms were not included. The final R value of 0.082 was computed with a data-to-parameter ratio of 10.3. This yields a goodness-of-fit of 1.597 and a maximum shift/esd of 0.013 for overall scale in the last cycle of refinement. A peak of 2.10 e/Å^3 was found as the largest feature on the final difference Fourier map. It was located 1.26 Å from Au(2). The weighting scheme used was $w = \sigma^2(F_o)^{-1}$. Corrections for anomalous

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dispersions were applied to all atoms.

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Supplementary Material Available: Tables of atomic coordinates, bond distances, bond angles, anisotropic thermal parameters, and crystal refinement data for $[Au_2(\mu\text{-}PP_3)_2]Cl_2$ and $Au_4Cl_4(\mu\text{-}PP_3)$ (19 pages); listings of observed and calculated structure factors (58 pages). Ordering information is given on any current masthead page.

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Tristrontium Dialuminum Hexaoxide: An Intricate Superstructure of Perovskite

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$Sr_3Al_2O_6$, obtained as a white powder by solid-state reaction between $SrCO_3$ and Al_2O_3, has been studied by X-ray and neutron diffraction. It is cubic, $a = 15.8425$ (2) Å, space group $Pa\bar{3}$, and $Z = 24$. Its crystal structure, refined from the neutron powder data on the basis of the $Ca_3Al_2O_6$ structural model, is described as a superstructure of the perovskites, ABO_3. Several features, such as oxygen and A deficiency and 1:3 B-cation ordering, which are present simultaneously, suggest that the formula must be rewritten as $Sr_{7/8}\square_{1/8}(Sr_{1/4}Al_{3/4})O_{9/4}\square_{3/4}$. Bond-valence values obtained for Sr atoms in the A and B subcells are discussed.

Introduction

The structure and composition of tricalcium dialuminum hexaoxide and related compounds are of considerable interest, since $Ca_3Al_2O_6$ (abbreviated to C_3A in cement chemistry), in an impure form, is one of the main components of Portland cement. This compound is cubic, $a = 15.263$ Å, space group $Pa\bar{3}$, and $Z = 24$. The structure[1] consists of rings of six AlO_4 tetrahedra (Al_6O_{18}), eight to a unit cell, surrounding holes of radius 1.47 Å, at $^1/_8$, $^1/_8$, $^1/_8$ and its symmetry-related positions, with Ca^{2+} ions holding the rings together.

$Sr_3Al_2O_6$ is isostructural with C_3A, as indicated by Lagerqvist et al. in an earlier work.[2] On the other hand, Büssem and Eitel[3] pointed out the similarity of the X-ray powder diffraction patterns of the Sr compound and that of perovskite ($CaTiO_3$, $a \approx 3.8$ Å). However, the possible relationship between these structures was not subsequently shown.

The ideal perovskite structure ABO_3 can be briefly described in terms of a cubic unit cell with $a_0 \approx 4$ Å, the smaller B cations being at the corners, the oxygens at the midpoints of the edges, and the larger A cations at the center of the cube. Deficient perovskites, in which A atoms and/or oxygens are partially lacking are well-known.[4] On the other hand, when the B sites are occupied by two different cations, an ordered arrangement between them is to be expected if their sizes or charges are different enough. A large number of perovskites showing 1:1, 1:2, and 1:3 B-cation ordering, with stoichiometries $A(B'_{1/2}B''_{1/2})O_3$, $A(B'_{1/3}B''_{2/3})O_3$, and $A(B'_{1/4}B''_{3/4})O_3$, respectively, have been described.[4,5] All these are superstructures of the perovskite, built up with two or more perovskite units and with unit cell parameters related to a_0.

The aim of this work is to report the crystal structure of $Sr_3Al_2O_6$ and to describe it as a superstructure of perovskite, in which several features (i.e. oxygen and A deficiency and B-cation ordering) are present simultaneously.

Experimental Section

Sample Preparation. $Sr_3Al_2O_6$ has been prepared as a white powder from a stoichiometric mixture of analytical grade $SrCO_3$ and Al_2O_3. The sample was ground and heated in air several times, in alumina crucibles, at increasing temperatures between 1073 and 1273 K, for 20 h each, and annealed at 1473 K for 10 h, in order to improve its crystallinity. After each thermal treatment the product was characterized by X-ray diffraction. Total weight losses corresponded to all CO_2 of the starting mixture.

Table I. General Parameters of the Two-Phase Rietveld Refinement

		$Sr_3Al_2O_6$	SrO
space group		$Pa\bar{3}$	$Fm\bar{3}m$
unit cell a param, Å		15.8425 (2)	5.1666 (3)
scale factor		0.00719 (5)	0.137 (7)
vol fraction		97.7 (7)	2.3 (1)
no. of reflcns		1218	15
Bragg R_I factor, %		5.46	4.26
Bragg R_F factor, %		3.29	1.92
profile R_p factor, %	5.30		
profile R_{wp} factor, %	6.88		
expected R_E factor, %	4.14		
no. of observns	2730		
no. of variables	63		

X-ray and Neutron Diffraction. The X-ray powder diffraction pattern was obtained in a Siemens Kristalloflex 810 generator, Cu Kα radiation ($\lambda = 1.540598$ Å), and D500 goniometer, by step-scanning from 10 to 154° in 2θ, in increments of 0.01° in 2θ and with a counting time of 1 s each step. Powdered W, $a = 3.16524$ (4) Å, was used as an internal standard.

The neutron powder diffraction data were collected in the high-resolution D2B[6] diffractometer at the ILL/Grenoble. The high-intensity mode was used to collect the spectrum, at 295 K. The wavelength, $\lambda = 1.594$ (1) Å, was selected by the 533 planes of a germanium monochromator. The sample was enclosed in a vanadium can of 8-mm diameter and 40-mm height. The 64 counters, spaced at 2.5° intervals, were moved by steps of 0.05° in the range $8° \leq 2\theta \leq 147.5°$.

The neutron diffraction pattern was analyzed by the Rietveld[7] method, using the Young and Wiles[8] profile refinement program. A pseudo-Voigt function was chosen to generate the line shape of the diffraction peaks. The coherent scattering lengths for Sr, Al, and O were 7.070, 3.449, and 5.805 fm, respectively.[9]

No regions were excluded in the refinement. Since the presence of small amounts of SrO (with rock-salt structure) was detected in the pattern, the profile refinement of the mixture was performed.

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